# THERMODYNAMICS

# WITH RELATIONS TO STATISTICAL MECHANICS

# AND WITH APPLICATIONS TO STEADY STATES

By

Richard C. Tolman

## Chapter I

## The Principles of Thermodynamics

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# FOREWORD

Dr. Tolman had planned to write a book on thermodynamics on his return from Washington after the war. Because of more pressing demands on his time from other activities, he had completed only the introductory chapter at the time of his death. Publication of the chapter in essay form did not seem appropriate to those of his friends who examined the manuscript, since by structure and organization it was clearly not intended for this purpose.

At the same time, it seemed desirable that Dr. Tolman's discussion of some of the fundamental concepts of the science of thermodynamics should be made available to his colleagues and friends, and perhaps to their students. After reading the manuscript, Robert Oppenheimer made the fortunate suggestion that a limited number of copies be prepared and sent to a group of Dr. Tolman's friends and colleagues. This suggestion has been adopted as the best solution to the problem of distribution.

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### 1. Introduction

It is the threefold purpose of this book, in the first place to give a short review of the principles of thermodynamics, in the second place to provide a brief outline of the relations of thermodynamics to statistical mechanics, and in the third place to present a theory of the thermodynamic behaviour of systems in steady states together with applications to some typical examples. The book is in no sense a complete treatise on thermodynamics, but does give an opportunity to present in one place a fairly coherent account of certain newer aspects of thermodynamic theory which seem to the writer of considerable importance.

In the present chapter, The Principles of Thermodynamics, we shall discuss the nature of thermodynamic systems and processes, present the two laws of thermodynamics which govern the behaviour of thermodynamic systems and then define and consider certain thermodynamic functions which will be needed later. The chapter will of course contain nothing new, but it will be convenient for our purposes - and perhaps useful for more general purposes - to have a condensed account of thermodynamic theory available.

In Chapter II, Statistical Mechanics and Thermodynamics, we shall outline the explanation of the phenomenological science of thermodynamics

in terms of the more abstract science of statistical mechanics, laying special stress on the relation of the second law of thermodynamics to the H-theorem, on the appropriateness of the canonical ensemble as representing a system in thermodynamic equilibrium, and on the statistical mechanical quantity sum-over-states as providing a convenient apparatus for the computation of thermodynamic quantities. In Chapter III, Thermodynamic Properties of Matter, we shall use appropriate expressions for the sum-over-states as a starting point for certain applications of thermodynamics to the properties of matter. And in Chapter IV, Thermodynamic Properties of Radiation, we shall use an expression for the sum-over-states of thermal radiation as the starting point for an exposition of the thermodynamic theory of radiation. This exposition will be made reasonably complete, since the theory of thermal radiation is unfamiliar to many scientists who commonly employ thermodynamics in their work, and since we shall specially need the results of the theory for our later applications.

In Chapter V, Thermodynamic Theory of Steady States, we shall present and discuss the relations governing the thermodynamic behaviour of systems in steady states. Such steady states are those in which the condition of the system of interest does not change with time, any matter and energy which flow into the system being balanced by matter and energy which flow out, and any entropy which flows into the system, together with that which is being produced within the system, also being balanced by the entropy which is flowing out. These steady states are in general quite different from the usually studied equilibrium states

of systems where all processes are thought of as carried out under equilibrium conditions. In particular it is to be emphasized that irreversible processes may be taking place in the interior of a system in a steady state which lead to a continuous production of entropy. Hence, as we shall see, the thermodynamic theory of steady states permits us in appropriate cases to give adequate treatment to irreversible processes, as contrasted with more familiar thermodynamic treatments where the emphasis is laid on reversible processes carried out maintaining equilibrium conditions. Although a number of applications of thermodynamics to steady states have been made in the past, there appears to be no previous recognition of the advantages of developing a coherent treatment of this part of thermodynamic theory.

There are a number of systems of physical, biological or industrial interest which are in at least approximately steady states and to which the above mentioned theory can be profitably applied. The remainder of the book, Chapter VI, Engineering Applications, Chapter VII, Thermoelectric Application, and Chapter VIII, Photochemical Applications, will be devoted to the treatment of some typical examples of systems in steady states.

With this brief introduction we may now commence our study of thermodynamics.

## 2. Thermodynamic Systems.

The science of thermodynamics is primarily concerned with changes in the state of a system which occur when its content of energy or of matter is changed by the transfer of heat, work, or matter across the boundary between the system and its surroundings. Before presenting the two laws of thermodynamics upon which the science is based, we must first discuss the nature of the subject matter which will be involved. In the present section we consider what is meant by a thermodynamic system; in the next section § 3 we make some general remarks about thermodynamic states and the kinds of variables that occur in thermodynamics; in the following section § 4 we discuss the kinds of thermodynamic processes which are involved in changes of state, with special emphasis on the distinction between reversible and irreversible processes; and finally in § § 5-9, we prepare for the statement of the two laws of thermodynamics, by giving special consideration to the five quantities, energy, work, heat, temperature and entropy which appear in those laws.

In the considerations of thermodynamics, it is essential to distinguish between the system and its surroundings. A thermodynamic system is that portion of the universe in whose states we are specifically interested, and the surroundings are those portions of the rest of the universe from which the system may receive matter or energy by flow across the boundary. This presupposes a sufficiently distinct, actual or ideal, bounding surface between system and surroundings, so that we can distinguish, at least with suitable approximation, between the matter and energy belonging to the system and that belonging to the surroundings.

When a particular problem is to be solved, the location of the boundary between system and surroundings may be chosen as is most convenient or illuminating for the task at hand. But once chosen the location of the boundary must not be inadvertently allowed to change in the course of the argument. A frequent pitfall for example is to confuse work done within the boundary by one part of the system on another, with work done across the boundary by the system on its surroundings.

It is sometimes convenient to introduce the terms,-isolated system to designate one which is shut off from its surroundings so that there can be no transfer either of energy or matter to or from the system, closed system to designate one which transfer of energy but not of matter is permitted, and open system one where transfer of matter as well as of energy is contemplated. Systems are designated as homogeneous or heterogeneous according as the matter in the system has uniform or non-uniform properties throughout. When the matter in a heterogeneous system exists in separate homogeneous regions having different uniform properties, we speak of the matter as present in different phases, e.g. solid, liquid or gaseous. The matter in one such phase gives an example of an open system since we must contemplate changes in its amount by transfer from other phases.

3. Thermodynamic States and Variables.

By the thermodynamic state of a system, we shall mean its physical condition, at any instant of interest, as described by specifying the values, for the system, of a sufficient number of variables of the kind employed in thermodynamic considerations.

With regard to the number of variables, whose values must be specified in order to specify the state of the system, this must be sufficient so that we can calculate therefrom the values of any other thermodynamic variables that apply to the system at the instant of interest. It is to be remarked in addition that this also proves to be sufficient so that we can predict therefrom later thermodynamic states of the system, in so far as this is made possible by the laws of thermodynamics. As a simple example of the possibility of using the values of a limited number of variables to specify the complete thermodynamic state of a system, we may take as a system of interest a given quantity of perfect gas at equilibrium in a container of a given volume. Thermodynamic variables which might concern us would then include the pressure, volume, temperature and energy of the gas. The specification of the values of any two of these, however, would be sufficient to determine the others since pressure, volume and temperature would be connected by a simple so-called equation of state - the perfect gas law $pv/T$ = constant -, and energy and temperature for a perfect gas would be connected by the simple equation $E$ = constant x $T$. It is also to be noted that the specification of state so given would be sufficient to predict the later thermodynamic state that would arise, for example, if the gas were allowed to expand under one or another set of specified conditions into a container of double the volume.

With regard to the kind of variables employed in thermodynamic conditions, it is to be emphasized that the science of thermodynamics purposely adopts a macroscopic phenomenological point of view which includes no reference to the ultimate atomic or molecular constitution of the

system which it discusses. Hence the thermodynamic variables are themselves all macroscopic in character and do not include microscopic variables, such for example as the positions or velocities of the individual atoms or molecules composing the system under consideration.

The thermodynamic variables may be classified for convenience into the following categories:- quantities specifying internal structure, external coordinates, mechanical quantities, and the specifically non-mechanical thermodynamic quantities which the science of thermodynamics has itself introduced. The quantities specifying internal structure include masses of material and chemical compositions, as could be determined for the system as a whole or for its parts by the ordinary methods of chemical analysis. The external coordinates are taken as quantities having values that are definitely established by external agencies without reference to the internal condition of the system, for example the volume of the system as determined by the position of a piston, or the coordinates locating external mechanisms which can exert fields of force on the system, or, the coordinates locating heat reservoirs which might be placed in thermal contact with the system. The mechanical quantities include as the most frequently used the energy content of the system, and the pressure which it exerts on the walls of its container. The non-mechanical thermodynamic quantities are temperature and entropy - and the various subsidiary variables defined with their help - which the science of thermodynamics has specifically invented for the treatment of problems on its own phenomenological level of abstraction.

We shall find the above division into categories helpful when we consider, later in Chapter II, the relations between quantities as specified

in thermodynamics and in statistical mechanics. In addition to quantities of the above nature which are determined by the state of a system, thermodynamics also makes use of quantities - especially of heat and work - which are determined by the kind of process which takes the system from one state to another.

4. Thermodynamic Processes - Reversibility and Irreversibility.

Before we can undertake our later presentation of the laws of thermodynamics, it will be necessary to discuss different kinds of thermodynamic processes by which changes in the state of a system may be brought about. In particular it will be profitable to consider somewhat fully the distinction between reversible and irreversible processes which is fundamental to an understanding of the second law of thermodynamics. We may begin by defining certain simple kinds of process which are often mentioned in thermodynamic discussions, before turning to our main task of discussing reversibility and irreversibility.

A spontaneous process is defined as one which occurs of its own accord in an isolated system without intervention from the outside. A cyclical process is one at the end of which the system has been returned to its original state. An adiabatic process is one which occurs without the transfer of heat across the boundary between system and surroundings. The term adiabatic has also sometimes been used (Ehrenfest's adiabatic principle) to characterize a purely mechanical process carried out at an infinitely slow rate; this seems a misleading extension of the original meaning. In addition to the above defined terms, phrases such as isopiestic, isothermal, isoentropic etc. are often used to designate processes where some particular variable such as pressure, temperature,

entropy etc. is kept constant throughout the course of the process. A reversible process is defined as having a character such that both system and surroundings could be returned to their original states at the end of the process, either by a reversal of the original steps or by an appropriate selection of further reversible steps. An irreversible process is defined as having a character such that system and surroundings could not both be returned to their original states. Thus a process which finally leaves both system and surroundings in their original conditions would be both cyclical and reversible. And a process which leaves the system in its original state but leaves irremovable effects in the surroundings would be cyclical but irreversible.

Reversible processes are idealized processes proceeding or carried out without any degradation of energy which would prevent the return of both system and surroundings to their original conditions. A reversible process may be regarded as the limiting process approached by an actual process as we reduce and then conceptually eliminate those aspects of the situation which lead to the degradation of energy.

Although a full understanding of the nature of energy degradation involves a complete appreciation of the consequences of the second law, some simple examples will help to make the idea clearer. Mechanical processes can be made to approach reversibility as we reduce the degradation of energy due to such causes as friction. Thus a frictionless pendulum would continue to carry out a succession of reversible cyclical vibrations. Electromagnetic processes can be made to approach reversibility as we reduce the degradation of energy due to such causes as electrical resistance. Thus an electric oscillator, consisting of a capacity

and inductance without resistance, and surrounded by a perfectly reflecting (resistanceless) metallic mirror, for the return of energy sent out in the form of electromagnetic radiation, would carry out reversible oscillations. Physical-chemical processes can be made to approach reversibility as we reduce the degradation of energy which accompanies changes that occur under non-equilibrium conditions. Thus the adiabatic expansion of a dissociating gas in an insulated cylinder could be carried out reversibily with the help of a frictionless piston allowed to move out against an external force, slowly enough so that the dissociating gas would always be in equilibrium with its products, and slowly enough so that the force exerted by the gas on the piston would always be in equilibrium with the external force, thus assuring the delivery of sufficient mechanical energy in the expansion to accomplish a later recompression to the original state without residual effects in the surroundings. It is to be noted that such an expansion would have to take place at an infinitessimal rate, and the need for infinitessimal rates is often characteristic of reversibility.

As will be appreciated from the foregoing, the actual processes which take place in nature are irreversible in character, since they are in general accompanied by degration of energy. Even the motion of the planets is slowed down by tidal actions. Common sources of energy degradation, some of which have already been mentioned above, include the effects of friction, inelasticity, electrical resistance, dissipation of electromagnetic radiation, free expansion of gases, free diffusion of one substance into another, free chemical reaction and free flow of heat through finite temperature intervals. Quantitative treatment of irreversibility resulting from energy degradation will be made possible by the second law of thermodynamics.

## 5. Energy.

The quantities energy, work, heat, temperature and entropy are the ones which occur in the mathematical statement of the two laws of thermodynamics. Hence an understanding of the concepts corresponding to these quantities is fundamental to an understanding of thermodynamics. We devote the next five sections to discussion of these quantities.

We shall denote the energy content of a system by the letter E. The concept of energy is taken by thermodynamics from ordinary mechanics modified to the extent of recognizing the existence of forms of energy which were not treated in simple mechanics. Hence the concept needs little discussion beyond the reminder that we regard the principle of the conservation of energy as an empirically valid law, and can always regard energy as transformable into - or at least from - some simple known form, such as the kinetic energy of a moving body, or the potential energy of a compressed spring, with whose measurement we are familiar.

The assignment of a definite value to the energy E of a system presupposes, as already noted, the existence of an appropriate boundary which makes it feasible to distinguish between the energy content of the system and that of its surroundings. It is to be emphasized that the energy content of a system will be treated as a definite function of the state of the system, since either the energy itself will be one of the variables used to specify the state or the other variables chosen will themselves be sufficient to determine the value of the energy.

## 6. Work.

We shall denote the work done by a system on its surroundings, when a change state takes place, by the letter W. The concept of work is

taken by thermodynamics directly from ordinary mechanics, the work done being the integral of the force exerted by the system with respect to the displacement of the point of application. Generalized expressions for force and displacement, such as pressure and change in volume, can of course be used for the calculation. It will be noted that W will be taken with the positive sign when work is done on the surroundings.

It is to be emphasized that the quantity W measures an amount of energy transferred between system and surroundings by mechanical action, but has no reference to the form in which that energy exists in the interior of the system. Thus the circumstance that W is to be calculated by integrating force by displacement does not imply that the energy transferred was present as potential energy within the system.

Unlike energy, work is not a quantity that is characteristic of the state of a system but rather one which characterizes some process by which a change in state takes place.

7. Heat.

We shall denote the heat absorbed by a system from its surroundings, when a change in state takes place, by the letter Q. Since the concept of heat transcends the consideration of ordinary mechanics its use in thermodynamics needs considerable discussion. From the macroscopic point of view of thermodynamics the quantity Q measures energy transferred from surroundings to system by non-mechanical processes which cannot be analyzed in terms of a macroscopic force times displacement. From the microscopic point of view of kinetic theory this transfer of energy may turn out to be brought about by disordered interactions taking place between molecules of the system and of the surroundings at the boundary surface where they

come into juxtaposition. Such a non-thermodynamic point of view may permit the analysis of heat transfer in terms of non-macroscopic molecular forces which thermodynamics, however, does not include in its considerations. Consideration of the methods of heat measurement, of the mechanical equivalent of heat, and of the conditions which lead to the flow of heat will have to be postponed to the next section §8, when we can make use of the concept of temperature. It will be noted that Q will be taken with the positive sign when the direction of heat transfer is from surroundings to system.

In analogy to remarks made in connection with the quantity W, it is to be emphasized that the quantity Q measures an amount of energy transferred between system and surroundings by non-mechanical action, but has no reference to the form in which that energy exists in the interior of the system. When energy is transferred to a system by the flow of heat, it may be possible from a kinetic theory point of view to follow the transformation of this energy into the kinetic energy of moving molecules, or the potential energy of molecules that have been dissociated into atoms, or the potential energy of molecules which have been evaporated from a condensed phase, or into some other form of energy. For example, in the isothermal expansion of a perfect gas against a conservative external force, the energy transferred into the gas by heat flow from the surroundings to keep the temperature constant, could be regarded as ultimately transformed into external potential energy associated with the displacement of the external force. But thermodynamics applies the term heat only to the energy as it is being transferred from surroundings to system by non-mechanical processes. This thermodynamic use of the term heat to

characterize energy undergoing a particular kind of transfer between systems and surroundings must be carefully distinguished from older uses of the term heat as designating an imponderable fluid or mode of motion existing in the interior of hot bodies. Indeed thermodynamic reasoning was often led astray by incorrectly regarding work W and heat Q as referring to energy inside the system, rather than to energy being transferred across the boundary by a particular kind of process. Heat like work is not a quantity that is characteristic of the state of a system but rather one which characterizes some process by which a change in state takes place.

For the correct application of thermodynamics, it is essential that the transfer of energy between system and surroundings should be properly classified into the two categories, work done W and heat absorbed Q. Since the distinction depends on the possibility or not of analyzing the energy transfer in terms of macroscopic force times displacement, and since this in turn depends on the scale of size of our observational and experimental apparatus, it might seem as though uncertainties and difficulties would be encountered in this connection. As a matter of fact such difficulties rarely arise, partly because of the great difference in the scale of molar and molecular phenomena, and partly because the good thermodynamist is careful to preserve throughout a given discussion a consistent point of view as to the scale of observational and experimental methods that he regards as permitted.

In concluding these remarks on heat and work it may be noted that the common conventions of taking heat as positive when it is absorbed by the system, and taking work as positive when it is done by the system,

has its historical origin in the early preoccupation of thermodynamics with applications to heat engines which are mechanisms for the transformation of thermal into mechanical energy, i.e., for the absorption of heat and production of work.

8. Temperature.

a. Thermal Equilibrium and Temperature Equality. We must now discuss the concept of temperature which is quite foreign to mechanics and must be regarded as an idea which the science of thermodynamics has itself introduced, for the treatment of problems on its own non-mechanical level of abstraction.

The general idea of temperature comes in the first instance from the response of our sense organs to bodies that we designate as hot or cold, that is, of higher or lower temperature. However, since our temperature sense is not very precise, and on occasion gives misleading results, some more finely quantitative and reliable method of determining temperature has to be introduced. For this purpose we make use of the circumstance, that the properties of any kind of matter - e.g., density-change with temperature, to provide a continuous scale of dependable numerical values that can be used to designate the different temperatures of a given material body, and we make use of our gross temperature sense to label the hot and cold ends of such a scale.

Although this method of determining temperatures has provided us so far only with temperature scales specific for each kind of material, it is nevertheless sufficient for investigating the temperature behaviour that results from thermal interaction. When two or more bodies, composed of the same or different materials, are left in thermal contact we find-

in general after a period of temperature adjustment in which some of the bodies have risen and others fallen in temperature-that a final state of thermal equilibrium is always reached in which the temperatures of all the bodies involved remain permanently constant.

This empirical discovery of the phenomenon of thermal equilibrium, for any number or kinds of bodies, makes it possible to deduce the following important theorem. If a given body A is found in separate tests to have the right temperature to be in equilibrium with each of two other bodies B and C, then these bodies will themselves have the right temperatures to be in equilibrium with each other, since otherwise a condition of thermal equilibrium could not exist for all three bodies A, B and C placed in contact together.

In accordance with the foregoing, it now proves convenient to introduce temperature scales which are not specific for each separate kind of material, by choosing one or another given kind of body or structure to act as a "thermometer", and then using values of some property of this thermometer to define the temperature of any other body with which the thermometer is brought into thermal equilibrium. Using such a thermometer, the theorem which was derived above then leads to the assignment of the same temperature to all bodies which are in thermal equilibrium with each other. In other words, equality of temperature now becomes the criterion for thermal equilibrium.

b. Perfect Gas Thermometer for the Measurement of Temperature. In the earliest thermometers constructed, changes in temperature were measured by changes in the volume of a given amount of a liquid or of a gas held under constant pressure. This form of thermometer

is still one of the commonest and most useful. Using such a thermometer, temperatures $\theta$ are taken as given in degrees Centigrade, by the volume of the fluid, measured on a scale of equal volume intervals, with zero on the scale chosen so as to correspond to the temperature of melting ice, and one hundred to the temperature of boiling water. The relation of temperature $\theta$ to volume of fluid v in such a thermometer is hence given by an expression of the form

$$\theta = 100\ \frac{v - v_m}{v_b - v_m}$$

$$= \frac{100v}{v_b - v_m} - \frac{100v_m}{v_b - v_m} \qquad (8.1)$$

where $v_m$ and $v_b$ are the volumes of the fluid at the melting point of ice and boiling point of water.

Thermometers of this kind, using different thermometric fluids, will in general give values of $\theta$ which agree exactly with each other only at the melting point of ice and boiling point of water, owing to differences in the thermal expansion of different fluids. Hence in precise work it is customary to specify the particular thermometric fluid used.

Among the different thermometric fluids that have been used, different gases under very low pressure, and hence at low concentration, have been found to give especially small discrepancies between the temperatures $\theta$ that would be assigned in accordance with (8.1) from measurements of their volumes v. Indeed, as the concentration goes to zero, these discrepancies are found to vanish completely. This arises for two reasons, in the first place, because it is found at sufficiently low concentrations that equation (8.1) can be expressed for any gas, at any specified pressure p in the form

$$\theta = \frac{pv}{NR} - 273.1 \qquad (8.2)$$

where N is the number of mols of gas and R is a universal constant, and, in the second place, because it is also found at sufficiently low concentrations that the ratio of the pressure volume product pv to the number of mols N has the same value for all gases at the same temperature. Hence at sufficiently low concentrations, values of $\theta$ become independent of the gas used in the thermometer.

As a consequence of the foregoing, we are now led to introduce the idea of a perfect gas as one which follows exactly the behaviour for gases of sufficiently low concentration that was described above, and are also led to introduce the idea of a perfect gas thermometer as one which makes use of such a perfect gas as its thermometric fluid.

Using temperatures as given by the perfect gas thermometer, the relation between the pressure, volume and temperature of a perfect gas can now be put in an extremely simple form. Rearranging (8.2) we have for a perfect gas

$$pv = NR(\theta + 273.1) \qquad (8.3)$$

where $\theta$ is in degrees centigrade. And defining the so-called Kelvin or absolute scale of temperatures T by the equation

$$T = \theta + 273.1 \qquad (8.4)$$

we then obtain for perfect gases the very simple equation of state

$$pv = NRT \qquad (8.5)$$

where T is in degrees Kelvin above the so-called absolute zero of temperature where the pressure-volume product would become zero.

The simplicity of this equation of state is due partly of course

to the circumstance that it expresses the properties of a perfect gas with the help of temperatures measured with a perfect gas thermometer. It is to be emphasized, however, that it is also due to an actual simplicity in the properties of perfect-i.e., sufficiently dilute-gases, since for all such gases we should have, as mentioned above,

$$pv/N = f(t) \qquad (8.6)$$

where temperature t could be measured on any selected temperature scale and the form of the function f would then be the same for all of the gases.

Henceforth, we shall regard the absolute or Kelvin scale of temperatures T, as the standard in terms of which all thermometric results are to be ultimately stated, and in terms of which all thermodynamic conclusions are to be expressed. This will have two advantages. In the first place, we shall now have a common language for stating temperatures, which for reasons of practical convenience are actually obtained from a variety of different kinds of thermometers, depending for example on electric resistance, thermoelectric power, emissivity, etc. as well as on volume. In the second place, owing to the simplicity of the gas laws $pv = NRT$ when expressed in terms of the absolute temperature T, we shall find that the second law of thermodynamics will itself assume a very simple form when expressed in terms of temperatures T.

In conclusion it is to be remarked that temperature T, unlike the quantities E, Q and W which we have previously discussed, is a quantity which has intensive rather then extensive magnitude.

c. Temperature Rise as a Measure of Heat Transferred. Having discussed the methods of temperature measurement, we may now inquire into the nature of the change in state which occurs when the temperature

of a substance is changed. For example, we may consider the change in state of a kilogram of water when its temperature is raised through one degree. It is found by experiment that such a change in state can be brought about in two different ways, either by mechanical action or by thermal action.

To raise the temperature of the water by mechanical action, we may arrange some form of stirring mechanism in the water which can be driven by the application of an external force. We then find, for small changes in temperature, that the rise in temperature of the water is proportional to the work done on the stirring mechanism, and hence to the energy dissipated in the water by the friction involved in stirring it. As a consequence, we may now conclude that the change in state which occurs when the temperature of a kilogram of water is raised through one degree is characterized by a corresponding definite increase in the internal energy of the water.

To raise the temperature of the water by thermal action, we may allow it to interact for a period of time with some body originally of higher temperature, for example a piece of heated copper. We then find, for small changes in temperature, that the rise in temperature of the water is proportional to the amount of copper used and to the drop in temperature of the copper which is found to accompany the process. Comparing with the result of the preceding paragraph, and making use of the idea of the conservation of energy, we must now conclude that the thermal action has consisted in the transfer of energy from the copper to the water, since the rise in temperature of the water through one degree is a change in state which is known to be accompanied by a definite increase in internal energy.

By considerations such as the foregoing, we are now led quite generally to the conclusion, that the process, which takes place when bodies of different temperature are allowed to interact thermally, consists in the transfer of energy from the hotter to the colder body. Furthermore, since this transfer of energy takes place by non-mechanical processes which cannot be analyzed in terms of a macroscopic force times displacement, we may say-in accordance with the definition of heat given in § 7--that the transfer takes place by the flow of heat from the hotter to the colder body. In later paragraphs we shall give further consideration to the nature of heat transfer, which can occur by conduction,by convection and by radiation.

For practical purposes it is convenient to measure quantities of heat in terms of the calorie as a unit. The calorie is defined as the quantity of heat which on absorption by water will raise the temperature of one gram of water from 15 to 16 degrees Centigrade. The so-called mechanical equivalent of this amount of heat is the quantity of mechanical work-expressed in mechanical units such as the joule-which would produce this same rise of temperature if introduced and dissipated in one gram of water, for example by the friction associated with stirring. Careful experiments to determine this quantity were first performed by Joule in 1843. The present best value of the mechanical equivalent of heat is taken as

$$1 \text{ calorie} = 4.182 \text{ joules} \qquad (8.7)$$

d. Temperature of Bodies not in Thermal Equilibrium. As we have seen above, when two bodies of originally different temperature are allowed to interact thermally, a process of heat flow is set up by which energy is transferred from the hotter to the colder body. This process

will continue until the final state of equilibrium is reached when both bodies will have the same temperature and further change will cease. We must now inquire into the significance that can be attached to the concept of temperature during the time when the bodies are not in a condition of thermal equilibrium, but are in the process of approaching that condition through the flow of heat.

The necessity for the suggested inquiry depends on the circumstance that the temperature of a body has been defined by the reading of a thermometer with which the body has come into thermal equilibrium. Hence the application of the concept of temperature in the absence of thermal equilibrium may well involve difficulties. For this reason, it will be noted that although we have applied the concept of temperature, in our previous discussions, to bodies in their original conditions of equilibrium before thermal interaction has been started and in their final conditions of equilibrium after temperature equality has been established, we have so far carefully avoided the application of the term to bodies between which heat flow is in progress.

That difficulties can arise in applying the concept of temperature to bodies, which are not in a condition of thermal equilibrium but are receiving or giving out heat, can be readily seen if we consider the results of attempting to measure the temperature of such a body with the help of one or another of the usual kinds of thermometer that might be actually employed. We then find that the temperature indicated by the thermometer reading depends in general (a) on time, (b) on the position in the body where the thermometer is applied, and (c) on the nature of the particular thermometer used. Some dependence of indicated temperature

on time and on position in a body where changes are taking place through heat flow, does not seem surprising and can be readily interpreted. The dependence of indicated temperature on the nature of the thermometer, however, seems more surprising and will need more elaborate consideration.

With regard to dependence on time, it seems reasonable, when two bodies of originally different temperatures are allowed to interact thermally, that the thermometer reading for the hotter one should gradually fall and for the colder one gradually rise since ultimately both bodies will arrive at one and the same temperature, intermediate between the temperatures from which they started. In any case, however, it is evident that a thermometer used to follow the changing temperature of a body would need to have its reading corrected for "lag" by an amount which would depend on the character of the particular thermometer used, since different thermometers would adjust themselves with varying amounts of delay to the changing condition.

With regard to dependence on position, it also seems reasonable, when two bodies or originally different temperatures are allowed to interact thermally, that thermometer readings should depend on position within the bodies, since it is clear that the ultimate attainment of thermal equilibrium will require energy transfer by heat flow not only between the two bodies but also between the different parts of each of them. In any case, however it is evident that a thermometer would need to have its reading corrected for "spread" by an amount depending on its size and character in order that it could be used to indicate temperature as a precise function of position.

With regard to the general question of the dependence of indicated temperature on the nature of the thermometer, the circumstance that the

corrections for "lag" and "spread" would themselves depend on the nature of the thermometer does not appear fundamental, since such corrections could presumably be correctly introduced empirically, for example by testing with smaller and smaller thermometers of the same general construction. The circumstance that does appear fundamental is the actual experimental finding that different kinds of thermometers, which indicate the same temperature when applied to a body in a condition of thermal equilibrium, can indicate different temperatures-even after proper correction for lag and spread-when applied at some point in a body which is not in a condition of thermal equilibrium.

The general explanation for this important finding depends on the fact that different kinds of thermometers respond with different sensitivity to different forms of energy. In a substance which has come to thermal equilibrium, the densities of different forms of energy will have adjusted themselves to definite equilibrium values, which depend on the substance and on the temperature. If, however, this substance is not in thermal equilibrium the densities of different forms of energy will be determined by the special circumstances concerned in the transfer of different forms of energy from place to place and their change from one form into another, and the values of the energy densities at any point in the substance will not in general be those that correspond to any particular equilibrium temperature. Hence, different thermometers that respond with different sensitivity to different forms of energy will now indicate different temperatures.

Some illustrations will help to make this clearer. In a region where energy is being transferred both by radiation and by conduction, a

thermometer which responds sensitively to radiant energy may read higher than one which responds primarily to the internal energy of the substance surrounding it. Thus a blackened thermometer bulb held outdoors in the sunlight leads to higher readings than a reflecting one, since the former responds to the sun's radiation and the latter to the surrounding air. In a fluid where transfer of energy is taking place through convection currents, a thermocouple subject to impact of the current would read higher than one protected therefrom as the result of the transformation of kinetic into internal energy. In wind tunnel operations, where to be sure the currents are due to mechanical rather than thermal action, it becomes very important to distinguish between the so-called "total" temperature of the air caught and adiabatically compressed in a little chamber, and the so-called "free flow" temperature that would be registered by a freely floating thermometer. In the case of chemical reaction which may be taking place in the absence of equilibrium conditions, a thermometer which catalyzes the reaction can read differently from one which does not, owing to the transformation of chemical energy into other forms of internal energy. Thus in hydrogen gas, which is cooling down in the region from 3500 to 2000 degrees, a resistance thermometer covered with platinum black would read higher than a bare one, since it would catalyze the recombination of monatomic into diatomic hydrogen. Additional illustrations can be given, in which the anomalies in thermometer readings would depend as above on anomalies in the distribution of energy between different energy forms ordinarily considered in thermodynamics, and also in which the anomalies would depend on anomalies in the distribution between different forms of molecular energy not considered in thermodynamics.

In view of these findings, it must be concluded in general that the concept of temperature loses, to a greater or lesser extent, its simple and definite character in the absence of thermal equilibrium. We shall find later reinforcement for this conclusion, in the next chapter, when we consider the statistical mechanical interpretation of the thermodynamic quantity temperature. Under the circumstances, it is evident that we must proceed with care in our use of the term temperature when applied in situations where heat flow is underway. In following paragraphs we shall consider procedures that may be adopted when it becomes desirable or necessary to use the term temperature in the absence of thermal equilibrium. One of these procedures is of considerable theoretical importance.

A useful and obviously correct method of proceding, when different kinds of thermometers indicate different temperatures, is to accompany the specification of temperature with a specification of the character of the thermometer used. Thus, returning to the earlier illustration of temperature measurements in the path of sunlight, we can speak of the temperature,-as measured with a perfectly reflecting but thermally conductive thermometer,-as measured with an absorbing but non-conducting thermometer,-or as measured with an absorbing thermometer provided with a lense for the concentration of the sun's rays. Such operational specifications of temperature can evidently not lead us into difficulties.

Another procedure, which is often employed in describing systems that are not in thermal equilibrium, is to ascribe different temperatures to different components of the system. This is often done with the help

of statistical mechanical correlations of temperature with the mean kinetic energy of molecules or with the energy and frequency of electromagnetic radiation.

In a region where violent disturbances are in progress, it may seem helpful for example to ascribe different temperatures to slow moving molecules of gas that may be present, to fast electrons shot in from outside, and to radiation of the different frequencies present. As another example, it has been found useful by Bohr to ascribe different temperatures to an atomic nucleus in different states of excitation. Such applications of the term temperature are sometimes convenient and profitable but are often unprecise and must be used with circumspection.

In a body which is not in thermal equilibrium, the discrepancies between the readings of different kinds of thermometer will depend on the degree of disturbance away from the condition of thermal equilibrium, and will tend to approach zero as equilibrium conditions are approached. When the discrepancies are small enough, looked at from the point of view of the particular problem under consideration, their existence is often disregarded. As an example, it is customary to say that heat will flow from a body of higher to one of lower temperature, without specifying the kind of thermometer used in measuring the two temperatures, and this is a correct statement if the discrepancies are small compared with the temperature interval between the two bodies. Indeed, when this temperature interval is a very large one, we can have experimentally quite appreciable discrepancies between the readings of different kinds of thermometers, corresponding to large disturbances

from conditions of thermal equilibrium in the bodies, and still get heat flow in the expected direction. As another example, it is customary in developing the theory of heat flow by conduction, to relate flow of heat and consequent temperature changes to the temperature gradient in the conducting medium, without specifying the kind of thermometer to be used for the measurement of temperature. This is a theoretically correct procedure as we go to the limit of zero heat flow, and a practically correct procedure even with very appreciable heat flow, owing to the small discrepancies that would actually be found between different kinds of indicated temperatures.

In concluding this account of the procedures that can be adopted when it is desirable to use the concept of temperature in the absence of thermal equilibrium, we may now consider a procedure that will prove to be important in connection with our later applications of the second law of thermodynamics. When heat is to be supplied by conduction from a heat reservoir, the degree of disturbance of the reservoir away from the condition of thermal equilibrium will depend not only on the rate of heat flow from the reservoir but also on the properties of the reservoir and of the substance filling it. As we increase the effective depth of the reservoir back of the surface through which heat is to be supplied, and increase the specific heat and the thermal conductivity of the substance from which the heat is to be drawn, it is clear from any given rate of heat supply that the substance filling the reservoir will approach a condition of constant uniform temperature throughout, or in other words will approach thermal equilibrium. Hence when the consequences of supplying heat to a system depend on the temperature at which the heat is supplied, it is sometimes desirable to regard the heat as being supplied from such

an idealized reservoir to which we can ascribe without ambiguity a definite equilibrium temperature. Similarly when heat is being conducted out of a system it is sometimes desirable to regard it as flowing into such an idealized reservoir. The concept of such idealized reservoirs, which can supply energy without appreciable disturbance away from the condition of thermal equilibrium at some specified temperature, also proves useful when we consider the theory of transmission of heat by radiation.

e. Temperature Difference as the Cause of Heat Flow Conduction, Convection, Radiation. We have seen in the foregoing that thermal equilibrium is brought about by the flow of heat from bodies of higher to bodies of lower temperature. In concluding our long discussion of the concept of temperature, it will now be appropriate to give a qualitative description of the different processes by which heat flow can take place when a temperature difference exists. For this purpose we shall distinguish between the mechanisms of conduction, convection, and radiation. We have already mentioned these mechanisms in the foregoing, but have postponed more complete description of them until we had investigated what measure of significance could still be attached to the ideas of temperature and temperature difference when heat flow is taking place. The following remarks ignore any difficulties as to the specification of temperature in the absence of thermal equilibrium.

In the case of conduction, the process of heat flow takes place between portions of matter which are in actual thermal contact. The transfer of energy is then brought about by direct interaction between

the matter on the two sides of the surface of contact, a process which from the non-thermodynamic point of view of kinetic theory could presumably be analyzed in terms of interactions arising from molecular motions and forces. The flow of heat at any point in the matter at any given instant of time can be represented by a vector $\bar{q}$ which gives the rate of heat transfer in units of energy per unit of area per unit of time.

In the case of heat conduction through the interior of an isotropic substance, having uniform properties or properties that vary continuously from point to point, it is found that the dependence of flow of heat on temperature can be represented by an equation of the form

$$\bar{q} = -K \text{ grad } T \qquad (8.8)$$

where the thermal conductivity K would be a constant for a substance of uniform properties, but in more general cases could depend on position and time, for example through its dependence on the composition and temperature of the substance.

In the case of heat conduction between two bodies, having different temperature $T_1, T_2$, through a surface of contact where there is an abrupt drop in temperature $T_1 - T_2$, it is found that the dependence of heat flow can be represented by an equation of the form

$$\bar{q}_v = h(T_1 - T_2) \qquad (8.9)$$

where $\bar{q}_v$ is the component of heat flow normal to the surface of contact, in the direction from the body at $T_1$ to the body at $T_2$, and h is a quantity depending on the properties of the substances composing the two bodies, which can be treated as a constant when wide variations in temperatures and in temperature differences are excluded,

In the case of convection, which is limited to fluid substances, so-called convection currents are set up by the action of gravity on portions of the fluid at different temperatures and hence of different densities. As a consequence of the currents, the transfer of energy by simple heat conduction may be augmented by a net transfer of internal energy from hotter to colder regions in the fluid. The nature of the convection currents that will be set up in any given case is so dependent on particular circumstances that a general treatment of the theory of convection is not feasible. However, the ultimate effect of convection is to aid the establishement of thermal equilibrium.

In the case of radiation, the process of heat flow is brought about, without actual thermal contact between the bodies involved, by the passage through intervening space of electromagnetic waves which transmit energy in accordance with the presence of the Poynting vector that accompanies their oscillating electric and magnetic fields. Transmission of energy by this mechanism will take place either through empty space or through matter which is sufficiently transparent for the frequencies involved. In order that the flow of heat between two bodies shall occur solely by the mechanism of radiation alone the intervening space must be empty, since the presence of matter between the bodies would lead to thermal contact which would also introduce flow of heat by the mechanism of conduction.

For the establishment of thermal equilibrium between two bodies of different temperature by the mechanism of radiation, we may think of them as surrounded by a perfectly reflecting mirror which will prevent the escape of radiation to infinity, and thus prevent the temperatures of

both bodies from dropping to zero. The process of establishing equilibrium will then be brought about by a net flow of radiation from the hotter to the colder body. In this process both bodies will emit energy quite independently in a manner depending on their temperatures and emission coefficients, and both bodies will abosrb part of the energy falling on them, in a manner depending on their absorption coefficients. However, on account of a necessary relation between the emission and absorption coefficients of a body the net transfer of energy will be in the expected direction from the hotter to colder body.

## 9. Entropy

We are now ready to consider entropy, the last of the five quantities which will appear in the mathematical statement of the two laws of thermodynamics. The concept of entropy like that of temperature is entirely foreign to mechanics, and is one which thermodynamics has itself introduced on its own level of abstraction for the treatment of its problems.

A full appreciation of the nature of entropy cannot be obtained until after a statement of the second law of thermodynamics. In a preliminary way, however, it may be said that entropy is a quantity which has been devised to provide a criterion for distinguishing between reversible and irreversible processes, and to provide an appropriate measure of the extent of the energy degradation which accompanies irreversible processes. When a reversible process takes place, the total entropy of the bodies involved in the process remains unchanged. When an irreversible process takes place, however, the total entropy of the bodies involved increases. Moreover, as we shall see later, the amount of the

entropy increase is directly related to the amount of work which would have to be provided from the outside in order to undo the energy degradation which accompanied the irreversibility.

Hence entropy is a quantity of the greatest importance for science. From a qualitative point of view, since the actual processes of nature take place in such a direction as to lead to the degradation of energy, increase in entropy becomes the criterion by which we can predict the direction in which actual processes can proceed. And from a quantitative point of view, since entropy increase is a measure of the extent of the degradation of energy that accompanies a process, it provides a measure of the extent to which the efficiency of a process has been cut down by energy degradation, and furnishes a goal which the efficiency may approach as the degradation is reduced.

The concept of entropy was first introduced by Clausius in the year 1850. In doing this he assumed the Carnot expression for the efficiency of an ideal heat engine as a possible valid formulation of the second law of thermodynamics, and then defined the quantity entropy in terms of quantities of heat and temperature that appear in that expression. Having thus based his definition of entropy on a prior statement of the second law, he could then show that entropy would have the useful properties which we have described above. This historical order of development is still often used in the presentation of thermodynamic theory.

In our mode of treatment, it will seem preferable to regard the second law of thermodynamics as a postulate which defines the quantity entropy and prescribes its properties. This we shall do immediately

after our statement of the first law of thermodynamics. Using this order of development we obtain at the start a very general formulation of the second law of thermodynamics, and then find that Carnot's expression for the efficiency of a heat engine can be derived as one of a number of important consequences of the second law of thermodynamics.

10. The First Law of Thermodynamics.

The first law of thermodynamics is an expression of the principle of the conservation of energy in a form which gives special recognition to the distinction between heat and work, so important in thermodynamic considerations. It may be stated in the form of the equation

$$\Delta E = Q - W \qquad (10.1)$$

where $\Delta E$ is the increase in the energy of a system accompanying a change in state, and $Q$ and $W$ are the heat absorbed by the system and the work done by the system, when the change in state takes place. The relation of this equation to the principle of the conservation of energy is evident, since it asserts that changes in the energy of a system must be equal to the net energy transferred across the boundary and cannot be brought about by the creation or destruction of energy within the system.

It is to be remarked that the change in energy $\Delta E$ is definitely determined by the particular change in state under consideration, since as already noted the energy of a system is a definite function of its state. The heat absorbed $Q$ and work done $W$, however, will depend on the particular process employed for obtaining the change in state under consideration, and it is only their difference which depends uniquely on the change in state.